

REMARKS

This paper is being provided in response to the August 28, 2001 Non-Final Office Action for the above-referenced application. In this response, applicant has amended claims 1-11 and 13-15 in order to more particularly point out and distinctly claim that which applicant deems to be the invention. Applicant respectfully submits that the amendments to the claims are all supported by the originally filed application.

The rejection of claims 1-11 and 13-29 under 35 U.S.C. §103(a) as being obvious over Tamaru et al (U.S. Patent No. 6,103,566, hereinafter referred to as "Tamaru") in view of Nishikawa et al. (U.S. Patent No. 6,087,261, hereinafter referred to as "Nishikawa") and further in view of Lee et al. (U.S. Patent No. 6,010,940, hereinafter referred to as "Lee") is hereby traversed and reconsideration thereof is respectfully requested. Applicant respectfully submits that the claims, as amended herein, are patentable over the cited references, whether taken separately or in any combination.

Claim 1, as amended herein, recites a method for forming a semiconductor device having a laminated structure of a dielectric film made from a metal oxide which is formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed on the metal oxide. The metal nitride film is directly formed on the dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained. The method has a step of treating the substrate in an ambient that is non-reactive with respect to the metal oxide film formed on the substrate in the chamber where the non-reactive ambient includes a gas non-

reactive with respect to the metal oxide and/or NH_3 gas. The method recites setting the temperature of the substrate at a prescribed temperature, before the source gas containing the high melting point metal is introduced into the chamber.

Claims 2 through 7, as amended herein, depend from claim 1 and recite further patentable features over the base claim. Dependent claim 2 recites that the non-reactive ambient treating step has a flow stabilizing step. Dependent claim 3 recites that the non-reactive gas is introduced during the flow stabilizing step. Dependent claim 4 recites that the treating step heats the substrate and the flow stabilizing step is after the heating step. Dependent claim 5 recites that the NH_3 gas is introduced into the chamber during the heating step. Dependent claim 6 recites that the NH_3 gas has a NH_3 partial pressure of no greater than 1.0 Torr and no less than 0.1 Torr. Dependent claim 7 recites that the non-reactive gas and the NH_3 gas are introduced into the chamber during flow stabilizing step.

Claim 8, as amended herein, recites a method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed. The metal nitride film is directly formed on the dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained. The method heats a substrate to a prescribed temperature in an ambient with an NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of the source gas containing the high melting point metal.

Claims 9-10, as amended herein, depend from claim 8 and recite further patentable features over the base claim. Dependent claim 9 recites a step of heating the substrate to a prescribed temperature and maintaining the temperature in a non-reactive gas, which is neither oxidizing nor reducing with respect to the metal oxide, and while the gas flow is stabilized. Dependent claim 10 recites that the NH_3 gas is introduced during the second half of the CVD film growing step.

Claims 11 and 13-29 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 11, as amended herein, recites a step that is performed before the CVD high melting point metal nitride film is formed, of heating the substrate (on which the dielectric film made for a metal oxide is formed) in the chamber while introducing the non-reactive gas. Then performing a step of forming the high melting point metal nitride film on the dielectric film by introducing a gas mixture comprising the NH_3 gas and the non-reactive gas, the non-reactive gas being in a volume amount that is larger than the NH_3 gas, and the source gas amount having less volume than the NH_3 gas. Dependent claim 13, as amended herein, recites that the dielectric film is a tantalum oxide (Ta_2O_5) film. Dependent claim 14, as amended herein, recites that the substrate is heated to between approximately 400°C and 700°C before the source gas containing the high melting point metal is introduced. Dependent claim 15, as amended herein, recites that the non-reactive gas is selected from a list of nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 16 recites that the high melting point metal nitride film is a TiN film. Dependent claim 17 recites that the source gas containing titanium is selected from the group consisting of titanium tetrachloride

(TiCl₄), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 18 recites that the high melting point metal nitride film is alternately a WN film, and WF₆ gas is introduced as a source gas. Dependent claim 19 recites that the device has a capacitive element, a dielectric film, a CVD high melting point metal nitride film as a protective film between the dielectric film and the capacitive element. Dependent claim 20 recites that the device has a MOSFET where the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer. Dependent claim 21 recites raising the partial pressure of the NH₃ gas during a second half of forming the CVD film on the metal oxide, so that annealing is done by the NH₃ gas. Dependent claim 22 recites that the dielectric film is a tantalum oxide (Ta₂O₅) film. Dependent claim 23 recites that the substrate is heated between approximately 400°C and 700°C. Dependent claim 24 recites that the non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 25 recites the high melting point metal nitride film is TiN. Dependent claim 26 recites the source gas containing titanium is selected from the group consisting of titanium tetrachloride (TiCl₄), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 27 recites that the high melting point metal nitride film is a WN film, and WF₆ gas is introduced as a source gas containing tungsten. Dependent claim 28 recites that the semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film between the dielectric film and capacitive element. Dependent claim 29 recites that the semiconductor device has a MOSFET with a gate insulation film and the CVD high melting point metal

nitride layer is the lowermost layer of the laminated gate electrode layer formed on the gate insulation film.

The cited art of Tamaru discloses a DRAM with a capacitive element that is protected from breakdown under the influence of a TiN film that is CVD deposited on the capacitor dielectric as a passivation film to prevent the dielectric from making any contact with the nitrogen containing reducing gas (please see col. 3, lines 25 - 49).

The Office Action indicates that the Tamaru reference shows that ammonia is a known ambient, and states on page 3 of the office Action that it “would have been obvious to one having ordinary skill in the art at the time the invention was made to have modified Tamaru’s vacuum pressure at less than 1 because a better non-reactive ambient can be obtained at the lower vacuum pressure”. Applicant respectfully disagrees with the suggestion in the Office Action that Tamaru describes or suggests a non-reactive ambient.

Applicant respectfully submits that the Tamaru reference teaches using an oxidizing titanium source gas ambient to form a metal layer prior to the introduction of any reducing gas such as ammonia, in order to prevent the disassociation of the metal oxide film by a reducing ambient. Thus the cited reference does not describe or suggest using a non-reactive ambient, as suggested incorrectly by the Office Action.

Tamaru discloses the use of ammonia to passivate (i.e., not a non-reactive process, but rather a nitridation process that forms a new material) the polysilicon lower electrode (col. 2, lines 10-24), and thus the suggestion in the Office Action that the use of ammonia in Tamaru represents a non-reactive ambient is incorrect. Applicant further notes that Tamaru contains no suggestion of any ammonia or reducing gas used after the dielectric is formed (col. 3, lines 30 -49; col. 4, line 20) until a oxygen containing titanium source gas has covered the metal oxide with the upper electrode (col. 18, lines 33- 40). The Tamaru reference states that the metal oxide should not come into contact with reducing gases such as ammonia, and thus directly teaches against the recited features of the claimed invention. Thus Tamaru is an inappropriate reference for a number of reasons.

The cited art of Nishikawa has been discussed in prior responses, and discloses a method of forming a dielectric film on a semiconductor substrate in a reduced pressure atmosphere, and then depositing a metal or metal nitride on the dielectric. Nishikawa discloses that hydrogen, carbon and methane released as a normal part of the CVD deposition causes electrical leakage in the dielectric film. Nishikawa discloses that this electrical leakage problem is reduced by using oxygen containing gases (i.e., oxidizing with respect to the metal oxide) in the formation of the conductor film (col. 2, lines 18-27; col. 4, line 66; col. 9, line 15). Nishikawa states that this oxygen containing step is extremely important (col. 2, line 63). Thus applicant respectfully requests the Examiner to explain the suggestion in the second paragraph on page 4 of the present outstanding Office Action, that Nishikawa teaches using an inert ambient.

The Nishikawa reference discloses that using a reaction gas that contains oxygen (i.e., not a non-reaction ambient with respect to the metal oxide) at up to 5 sccm (col. 5, line 23) produces an oxygen containing metal film (i.e., a film that has been oxidized - a process that one of ordinary skill in the art would clearly recognize as not occurring in a non-reactive ambient) that does not have too high a resistivity to be a useful conductor. Thus the cited reference clearly teaches an ambient that is reactive.

Applicant respectfully submits that the suggestion on page 4 of the outstanding Office Action that “the limitation of non-reactive with respect to the metal oxide is not consistent with the claimed invention” is incorrect. The specification at page 1 and page 4 last paragraph, discusses the problem of leakage due to reactive gases on tantalum oxide film. In the section of the specification that deals with the experimental measurements made on the metal oxide leakage, the application notes on pages 7 and 8 and in table 3, that if the ammonia partial pressure is less than 1 Torr, the ammonia ambient is non-reactive with respect to the metal oxide. Thus, the suggestion in the Office Action that the claim language is inconsistent is clearly incorrect since the language and experimental facts supporting the claims language may be found in the specification, and this fact has been discussed previously in Applicant's last two responses.

Applicant respectfully submits that the cited Nishikawa reference teaches an oxidized metal that is not too resistive. Nishikawa does not teach a non-reactive ambient

protecting a metal oxide layer that is used as a dielectric in a capacitor. Nishikawa teaches moderately high resistivity conductors versus the dielectric (i.e., a non conductor) of the present invention. Nishikawa teaches using an oxidizing ambient to form a slightly oxidized metal layer, in order to prevent the destruction of the film by a reducing ambient. Thus, applicant respectfully submits that the cited reference of Nishikawa teaches using copious amounts of an oxidizing ambient, and can not provide motivation for one of ordinary skill to use a non-reactive ambient. Thus Nishikawa is also an inappropriate reference for a number of reasons.

The cited art of Lee discloses a method for making a TiN barrier for the upper plate of a capacitor to reduce the reactions between the metal oxide and the polysilicon upper electrode (col. 1, line 26). The TiN layer is disclosed as being formed using TiCl_4 , which may form chlorine that may attack the metal oxide. The chlorine is reduced by use of an ammonia anneal which chemically attacks the chlorine (i.e., not a non-reactive ambient) and removes it as HCl gas. The anneal step is disclosed as occurring after the TiN deposition and not prior to metal deposition and thus not having any possible impact on the metal oxide layer, since one of ordinary skill would know that a metal layer is a barrier to chemical attack on the metal oxide dielectric layer below. Thus the Lee reference can not supply any motivation for one of ordinary skill to combine with references that oxide the substrate.

Applicant's independent claim 1 utilizes an inert ambient, which is clearly different from the cited reference. Specifically, independent claim 1, as amended herein,

recites that “...*said method comprising a step of treating said substrate in an ambient that is non-reactive with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH_3 gas* ...”, which is not suggested by any possible combination of the oxidizing ambient of the cited reference of Nishikawa, the TiN barrier of Lee, or the ammonia nitridation reaction of Tamaru. Independent claim 8 recites that “...*heating a substrate onto which said dielectric film is formed to a prescribed temperature in an ambient having a NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of said source gas containing said high melting point metal* ...”, which, for the same reasons given above with respect to claim 1, is neither described nor suggested by any combination of the cited references.

Applicant submits that if the ambient of the cited reference is intended and stated unambiguously by the cited reference to oxidize or nitride a layer, then it can not be non reactive towards the layer, as required in the claimed invention. There is no non-reactive ambient found in any of the suggested references, and thus even if there were some motivation to combine the references, the combination still does not provide the features of the present invention.

That the cited reference of Nishikawa teaches using an oxidizing ambient and thus not an ambient that is non reactive with respect to the underlying metal oxide is clear since the stated goal of the cited reference is to use the oxidizing gas to form (i.e., not a

non-reactive ambient) the oxygen containing conductor film. The Nishikawa reference explicitly states that the stabilization of the dielectric film obtained by using “the copious supply of the oxidizing gas” (col. 2, line 58) to prevent “deficiency of oxygen” (col. 1, line 62) in the dielectric film is “extremely important” (col. 2, line 63), thus clearly not suggesting use of a non oxidizing gas such as in the claimed invention. Applicant believes that this makes it clear to one of ordinary skill that the ambient used is non reactive with respect to the metal oxide rather than being absolutely inert in all respects.

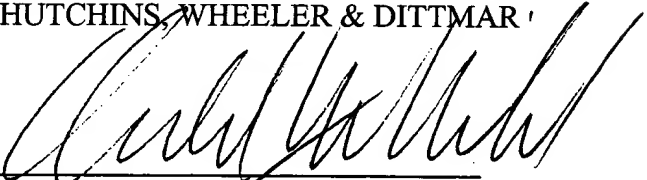
Applicant further respectfully submits that the Lee reference discloses an anneal process that occurs after a TiN barrier layer is formed, and thus does not describe or suggest an anneal of the metal oxide, since the barrier is stated to protect the metal oxide. Lee teaches a method of chemically removing residual chlorine gas in a vacuum system. Applicant respectfully submits that such a reference does not provide motivation for one of skill in the art to combine with other cited art since it does not teach protecting the metal oxide film from reducing ambients as disclosed in the cited references.

Therefore, applicant respectfully submits that independent claims 1 and 8, as amended herein, are not obvious over the suggested combination of cited references, specifically that the suggested combination of references discloses the use of oxidizing or nitridating ambients that are reactive to the underlying metal oxide layers and thus have barriers. Dependent claims 2-7, 9-11 and 13-29 are held to be patentable at least as depending from base claims shown above to patentable over the suggested combination of references.

Therefore, for reasons set forth above, applicant respectfully requests that this rejection be reconsidered and withdrawn.

Based on the above, applicant respectfully requests that the Examiner reconsider and withdraw all outstanding rejections and objections. Favorable consideration and allowance are earnestly solicited. Should there be any questions after reviewing this paper, the Examiner is invited to contact the undersigned at 617-951-6676.

Respectfully submitted,
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1. (Thrice Amended) A method for forming a semiconductor device having a laminated structure including a dielectric film made from a metal oxide [which is] formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained,

said method comprising a step of treating said substrate in an ambient that is non-reactive with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH_3 gas,

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wherein a temperature of said substrate is set at a prescribed temperature, before said source gas containing said high melting point metal is introduced into said chamber.

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2. (Twice Amended) The method for forming a semiconductor device according to claim 1, wherein said non-reactive ambient treating step includes a flow stabilizing step for a gas flow in said chamber.

3. (Twice Amended) The method for forming a semiconductor device according to claim 2, wherein said non-reactive gas portion of said non-reactive ambient treating step is introduced into said chamber during said flow stabilizing step.

4. (Twice Amended) The method for forming a semiconductor device according to claim 1, wherein said non-reactive ambient treating step includes a step for heating said substrate to a predetermined temperature, and said flow stabilizing step is performed after said heating step has been completed and said predetermined temperature has stabilized for a predetermined length of time.

5. (Twice Amended) The method for forming a semiconductor device according to claim 4, wherein said NH_3 gas portion of said non-reactive ambient is introduced into said chamber during said heating step.

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6. (Twice Amended) The method for forming a semiconductor device according to claim 5, wherein said NH_3 gas portion of said non-reactive ambient has a NH_3 partial pressure atmosphere of no greater than 1.0 Torr and no less than 0.1 Torr.

7. (Twice Amended) The method for forming a semiconductor device according to claim 5, wherein said non-reactive gas and said NH_3 gas portions of said non-reactive ambient are introduced into said chamber during said flow stabilizing.

8. (Twice Amended) A method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained, said method comprising:

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heating a substrate onto which said dielectric film is formed to a prescribed temperature in an ambient having a NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of said source gas containing said high melting point metal.

9. (Twice Amended) The method for manufacturing a semiconductor device according to claim 8, said method further comprising prior to the introduction of said source gas:

a step of heating said substrate to a prescribed temperature; and

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a step of maintaining said substrate temperature in a gas ambient that is non-reactive and neither oxidizing nor reducing with respect to said metal oxide and the flow thereof is stabilized; and

said NH_3 gas being introduced during at least one of said substrate heating step and said flow stabilization step.

10. (Once Amended) The method for manufacturing a semiconductor device according to claim 9, said method further comprising;

a step of introducing said source gas containing said high melting point metal, and growing a CVD high melting point metal nitride film after performing said flow stabilization step; and

a step of raising the partial pressure of the NH_3 gas during a second half of the CVD film growing step so that annealing of said nitride film by the NH_3 gas occurs.

11. (Thrice Amended) The method for manufacturing a semiconductor device according to claim 1, said method further comprising;

a step, performed before said CVD high melting point metal nitride film forming step, of heating a substrate onto which said dielectric film made from a metal oxide is formed, in said chamber while introducing therein said non-reactive gas; and

a step of forming said high melting point metal nitride film on said dielectric film made from a metal oxide by introducing a gas mixture comprising said NH_3 gas and said non-reactive gas, said non-reactive gas in an amount equal to or larger than said NH_3 gas, and said source gas containing said high melting point metal in a volume amount that is less than said NH_3 gas

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13. (Twice Amended) The method for forming a semiconductor device according to claim 1, wherein said dielectric film made from a metal oxide is a tantalum oxide (Ta_2O_5) film.

14. (Twice Amended) The method for forming a semiconductor device according to claim 1, wherein said substrate is heated to a temperature between approximately 400°C and 700°C before said source gas containing said high melting point metal is introduced into said chamber.

15. (Twice Amended) The method for forming a semiconductor device according to claim 1, wherein said non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases.

Claims not amended herein as believed to be currently constituted.

16. (Once Amended) The method for forming a semiconductor device according to claim 1, wherein said high melting point metal nitride film includes a TiN film.

17. (Once Amended) The method for forming a semiconductor device according to claim 16, wherein said source gas containing titanium as said high melting point metal, is a gas selected from the group consisting of titanium tetrachloride (TiCl_4), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT).

18. (Once Amended) The method for forming a semiconductor device according to claim 1, wherein said high melting point metal nitride film includes a WN film, and wherein WF_6 gas is introduced as a source gas containing

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19. (Once Amended) The method for manufacturing a semiconductor device according to claim 1, wherein said semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film disposed between said dielectric film and said capacitive element.

20. (Once Amended) The method for manufacturing a semiconductor device according to claim 1, wherein said semiconductor device has a MOSFET with a gate insulation film of a dielectric film, and wherein said CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer formed on said gate insulation film.

21. The method for manufacturing a semiconductor device according to claim 1, further comprising:

raising the partial pressure of the NH_3 gas during a second half of forming said CVD film on said metal oxide, so that annealing is done by the NH_3 gas.

22. The method for forming a semiconductor device according to claim 9, wherein said dielectric film is a tantalum oxide (Ta_2O_5) film.

23. The method for forming a semiconductor device according to claim 9, wherein said substrate is heated to said prescribed temperature between approximately 400°C and 700°C .

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24. The method for forming a semiconductor device according to claim 9, wherein said non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases.

25. The method for forming a semiconductor device according to claim 10, wherein said high melting point metal nitride film comprises a TiN film.

26. The method for forming a semiconductor device according to claim 25, wherein a source gas containing titanium as said high melting point metal, is a gas selected from the group consisting of titanium tetrachloride (TiCl_4), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT).

27. The method for forming a semiconductor device according to claim 10, wherein said high melting point metal nitride film comprises a WN film, and wherein WF_6 gas is introduced as a source gas containing tungsten.

28. The method for manufacturing a semiconductor device according to claim 8, wherein said semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film disposed between said dielectric film and said capacitive element.

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29. The method for manufacturing a semiconductor device according to claim 8, wherein said semiconductor device has a MOSFET with a gate insulation film of a dielectric film, and wherein said CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer formed on said gate insulation film.
